

Available methods for isolating, identifying, and tracing to their sources of origin the organic chemicals polluting our water supply are reviewed.

Organic Contaminants Affecting the Quality of Water

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TODAY'S vast chemical industry and particularly its giant offspring, the production of synthetic organic chemicals, have introduced new problems to scientists engaged in providing and protecting the Nation's supply of pure water. By one route or another, these chemicals or the waste products resulting from their manufacture enter the natural environment and affect the water adversely not only for the householder but even for further industrial use. Many of the products, particularly the synthetics, were unheard of a few years ago. Recent and estimated production rates of several of these chemicals are shown in table 1 (1, 2).

Industrial contamination of water, while important, is not the only factor to consider in the complex organic pollution situation. Domestic sewage, natural run-off, and materials derived from the life cycle of aquatic plants and animals contribute substantial quantities of organic materials to streams. Increased supplies of phosphorus and nitrogen from sewage

and other sources may stimulate extensive growth of algae or other aquatic life. Artificial water impoundments also may promote the growth of objectionable organisms.

The complexities of disposal of wastes from the production of organic chemicals have been described by Hess and Carney (3). The residues from large diversified manufacturing processes may contain thousands of complex compounds including byproducts, process aids, unreacted raw materials, and the manufactured product itself. The volume of these wastes may be as large as that of the main product. Effective treatment methods for many of these complex materials remain to be developed. Even when practical and economical treatment has been devised, complete elimination may be impossible.

Effects on Water Supplies

The effects of the diverse mixtures of organic materials on each other, on water, and on the consumer of drinking water are only beginning to be appraised. Among those known are the production of taste and odor in water and interference with treatment of water for industrial and domestic use. Costly ion exchangers deteriorate under the attack of organic chemicals in water (4). Acids are suspected. Polynuclear hydrocarbons possessing carcinogenic

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Table 1. Recent and estimated production of certain synthetic organic chemicals, in millions of pounds

Year	Detergents	Plastics	DDT	Organic agricultural chemicals	
				Benzene hexachloride	Toxaphene, chlordane, aldrin, and dieldrin
1947			560	8	
1950	1, 660	2, 280		75	40
1952			105	160	115
1955	2, 000	3, 500	125	170	
1960	2, 500	4, 800	155	200	
1975	4, 000	9, 000	200	225	

characteristics were detected by Wedgewood (5, 6) in waste effluents of domestic and industrial origin. An extensive review of the literature on the toxicity of materials known to be discharged into water has been initiated (7).

Taste and odor in drinking water, the most obvious contaminating effect of organic chemicals, is a widespread problem of considerable significance and causes more consumer distress than any other factor in water plant operation. In a 5-year period (1948-52) chemical costs for the control of tastes and odors at the South District Filtration Plant in Chicago (8) amounted to \$462,000, equivalent to 21.7 percent of the total chemical cost. More than 1,000 water plants in the United States use active carbon for the control of taste and odor. While carbon treatment and other methods for controlling these objectionable conditions have been developed, difficulties are frequently such that the required treatment cannot be provided.

An indirect effect on health arises when unpalatable water causes the consumer to seek other drinking water sources—even bacterially contaminated ones.

Isolation and Identification

The organic chemicals occurring in water are usually present in very low concentrations, but a few parts per billion (p.p.b.) of contaminants may produce significant taste and odor. One part per billion is equivalent to a teaspoonful of material in 1 million gallons of water.

The low concentrations, complexities, and

varieties of organic pollution in water make the recovery and identification of these substances difficult. Specific methods, with few exceptions, for the analysis of the multitude of organic chemicals in water are lacking. Furthermore, ordinary analytical techniques are usually inapplicable to the extremely low concentrations which must be studied. Some means of concentrating the materials for analysis is necessary. Methods for concentrating, isolating, and identifying these materials have been under study by the Public Health Service at the Robert A. Taft Sanitary Engineering Center. Exploiting the unique adsorptive properties of active carbon, a filter has been developed which adsorbs most organic material from water. After water or wastes in quantities from 100 to several thousand gallons pass through the filter, the carbon is dried and the organic materials are extracted with chloroform or other organic solvent in a Soxhlet extractor.

The organic substances recovered from the carbon differ with the type of solvent used for the extraction. Chloroform, the solvent used in most studies, has been found to recover those substances principally responsible for undesirable taste and odor in water. Alcohol will remove a quantity of material equal to or greater than the amount recovered by the chloroform even after preliminary extraction by chloroform. These highly water-soluble materials recovered by alcohol appear to have relatively little significance as taste and odor factors. Most materials investigated for their taste and odor effects are adsorbed quantitatively by carbon, but desorption by chloroform is only 65 to 80 percent complete. Following extraction, the solvent is removed by distillation, and the residue is subjected to further analysis. Liquid-liquid extraction methods also have been utilized for concentration of materials from some effluents.

Details of the use of the carbon filter (fig. 1) and certain applications, particularly to taste and odor studies, have been described (9, 10).

Raw and Finished Water Studies

Raw and finished waters have been sampled by means of the carbon filter in several locations and under various conditions of pollution.



Figure 1. Bank of carbon filters used for collecting small concentrations of organic materials from water. Several thousand gallons of water are passed through these filters which adsorb organic contaminants from the water. The recovered materials are then analyzed for chemical content.

Table 2 lists the concentrations of organic materials recovered by chloroform extraction of the carbon. These materials are frequently sticky, brown semisolids having strong disagreeable odors resembling paint or varnish. Some of the samples show distinct oil layers.

It is significant that the organic materials survive standard water treatment processes and in many instances appear in the finished water in concentrations equal to those found in the raw water.

Little information is gained from the com-

Table 2. Recovery of organic materials from various waters by the carbon filter method

Location	Number of samples	Water source	Sample source	Type of pollution	Recovery of organic materials (parts per billion)		
					Maximum	Minimum	Average
Cincinnati, Ohio---	38	Ohio River-----	Finished water---	Sewage and industrial waste.	630	79	220
Nitro, W. Va.-----	14	Kanawha River--	Raw water-----	Chemical waste-----	3,060	170	930
Columbus, Ohio-----	3	Scioto River-----	do-----	None-----	82	38	62
Piketon, Ohio-----	2	do-----	do-----	Sewage and industrial waste.	606	587	597
Wyandotte, Mich.--	4	Detroit River----	Finished water---	Industrial waste and sewage.	336	38	203
Saginaw, Mich.----	1	Lake Huron-----	do-----	None-----	-----	-----	25

plex residue without further chemical separation. Utilizing solubility differences, the materials are separated into the broad groups of water-solubles, acids, bases, neutrals, and phenolic materials. The distribution by groups of the chemicals recovered from various waters is shown in table 3.

The neutral materials, whether the pollutants are of industrial or natural origin, generally constitute the most abundant group. Since neutral substances are less reactive than other classes of compounds, they can be expected to resist biological and chemical attack to a greater degree. However, even hydrocarbons that are quite stable chemically may be attacked biologically. Neutral compounds which may occur in water are aliphatic and aromatic hydrocarbons and their halogen derivatives, alcohols, aldehydes, ketones, ethers, esters, nitro compounds, amides, nitriles, sulfides, and many others. The neutral substances are frequently sources of intense odor which can be detected when only a few parts per billion are present.

Hydrocarbons and Related Materials

Aliphatic and aromatic hydrocarbons have been consistently isolated from drinking waters obtained from sources in the vicinity of petroleum refinery waste outfalls. These materials survive water treatment processes in concentrations sufficient to cause serious impacts on taste and odor. Associated with these materials are sulfur compounds, probably cyclic sulfides, also responsible for odor in water. A study of taste and odor components in refinery effluents and a method for identifying petroleum wastes in surface waters have been published (11, 12).

As much as 1 p.p.m. of organic material was recovered in the drinking water of a city located 10 miles below an area containing a concentration of chemical industries. Materials found include substituted benzene compounds, kerosene, polycyclic hydrocarbons, and phenyl ether. Intense odor was a pronounced characteristic of the recovered materials. The phenyl ether recovered was detectable by odor tests at a concentration of 5 p.p.b.; the pure laboratory reagent at 13 p.p.b.

Phenolic compounds have long been recog-

nized as being detrimental to water quality, particularly from the standpoint of taste and odor. These compounds are associated with waste products from coke plants, oil refineries, and other industries. The taste and odor intensity of many phenolic substances is increased several hundredfold when reacted with the low concentrations of chlorine ordinarily used at the water treatment plant. A 1 p.p.b. concentration of the chlorinated materials may be detectable by taste and odor. However, phenolic pollution is more amenable to control at the water plant than other types of pollution.

Petrochemical wastes have presented problems recently. No standard definition of the term "petrochemical" is available but the book "Petroleum Processing" suggests:

PETROCHEMICAL, *n.*: A chemical compound or element recovered from petroleum or natural gas or derived in whole or part from petroleum or natural gas hydrocarbons, and intended for chemical markets.

Included in this group are such familiar chemicals as alcohols, benzene, ammonia, carbon black, acetone, aniline, styrene, and sulfur. Wastes from the manufacture of these materials are complex and highly odorous. Where wastes are discarded into streams without adequate treatment, outbreaks of intense taste and odor have occurred. On one occasion, under winter conditions, the taste and odor were reported to have traveled 1,000 miles. The waste materials responsible were recovered from drinking water 400 miles from the point of discharge and were partially identified.

The development of the petrochemical industry has come about almost entirely since 1940. It is estimated that, at present, there are over 300 petrochemical plants (13) in operation in this country. In 1954, this industry produced 27 billion pounds of petrochemicals comprising approximately 25 percent of the total chemical production.

The rate of expansion of petrochemical production indicates that in 1965 this industry will be the source of half the chemicals produced in the United States. The extensive uses of petrochemicals derived from crude oil and natural gas cracking are summarized in the inset (p. 1130).

Nitriles have been isolated from drinking

Table 3. Chemical groups separated from carbon filter extracts of water samples taken from seven sources

Chemical group	Source, location, and type of water sample						
	Scioto River, Columbus, Ohio (tap)	Scioto River, Piketon, Ohio (raw)	Ohio River, Cincinnati, Ohio (tap)	Lake St. Clair, Mount Clemens, Mich. (raw)	Lake Michigan, Waukegan, Ill. (raw)	Big Sandy River, Catlettsburg, Ky. (raw)	Activated sludge sewage treatment plant, Richmond, Ind. (effluent)
Ether insoluble			6.2				
Water soluble		10.2	24.3	2.2	15.4	8.6	
Amine	5.5	2.4	3.2	1.6	4.3	2.4	8.6
Weak acid	12.1	6.2	16.7	17.2	20.4	14.0	30.0
Strong acid	12.1	11.3	14.0	13.0	7.9	13.4	21.8
Neutral	70.5	69.9	37.2	66.0	53.0	62.0	39.4

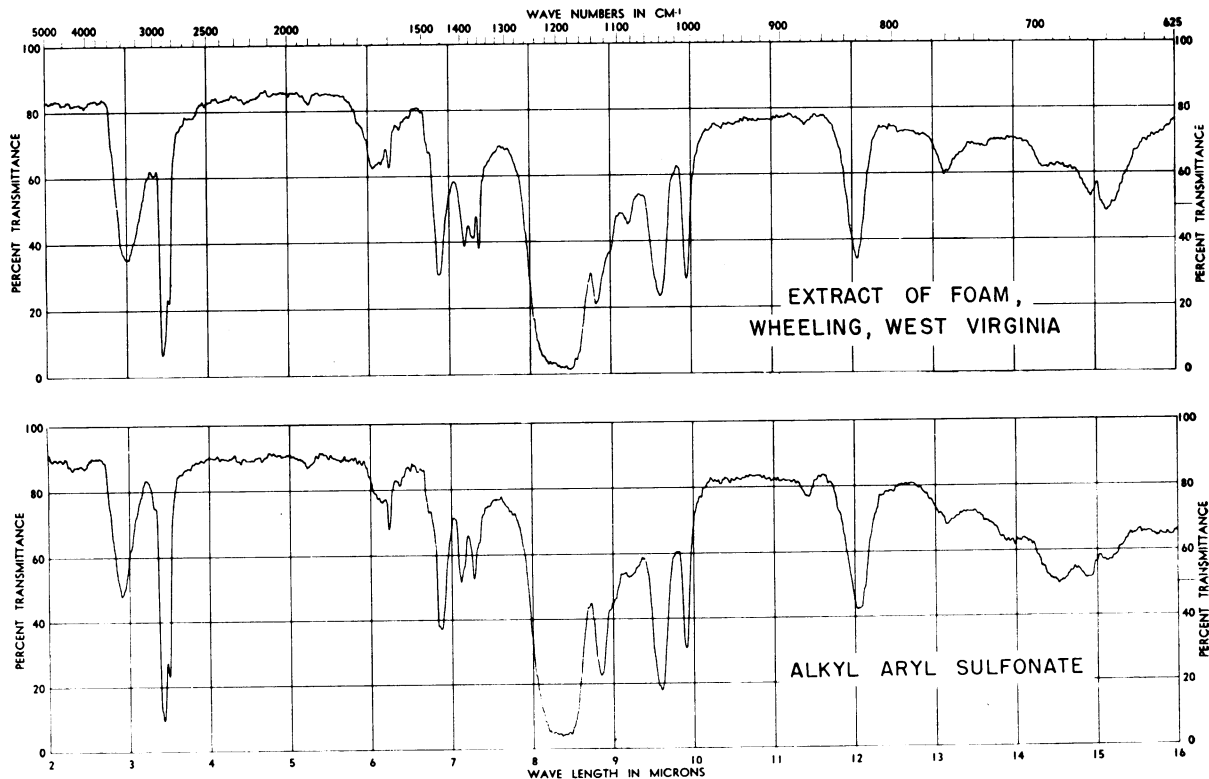
water in an area well known for the manufacture of petrochemicals. Acrylonitrile was indicated to be a component by infrared tests. While the toxicity of these organic cyanogen compounds is not great compared to the alkali cyanides, their presence in drinking water merits further study. Alcohols, aldehydes,

ketones, acids, and esters have been found in various waters. Some of these appear to be of industrial origin while others may be naturally produced.

Insecticides

Concentrations of DDT in the range of 1 to 5 p.p.b. were found in the drinking water of sev-

Figure 2. The similarity of these infrared spectrums indicate that foam material from the raw water at Wheeling, W. Va., contained large amounts of anionic synthetic detergents.



eral cities using rivers as sources of supply. The insecticide could not be recovered at all times but persisted for a 6-month period in one location. The major source of the DDT was presumed to be spray operations.

Through the widespread agricultural use of

DDT, exposure resulting from various sources (14, 15), particularly food, is much higher than the exposure that could result from ingesting drinking water containing a 5 p.p.b. concentration, the estimated maximum level found in the waters examined. Although present levels of

Basic Petrochemicals and End Products

CRACKING

OXIDATION

OTHER CHEMICAL TREATMENT

of crude oil and natural gas

give methane ethane propane butane ethylene acetylene
butadiene naphtha butylene propylene cyclopentadiene
isoprene isobutylene benzene cyclohexane

which **synthetic fibers**
acetates acrylics polyesters
nylons vinyls

are **synthetic rubbers**
butyl GR-S types neoprene
nitrile polyurethane types

used **plastics, resins**
alkyds epoxys phenolics polyesters
to polyethylene styrenes vinyls

make **automotive chemicals**
antifreezes hydraulic fluids oil additives
tetraethyl lead fluid other gasoline additives

also these other important end products

alcohols detergents drugs explosives glycerin ketones
miscellaneous solvents nitrogen fertilizers pesticides
plasticizers protective coatings refrigerants rocket fuels

SOURCE: *The Chemical Industry Facts Book, 2d Ed., Manufacturing Chemists Assoc., Inc.*

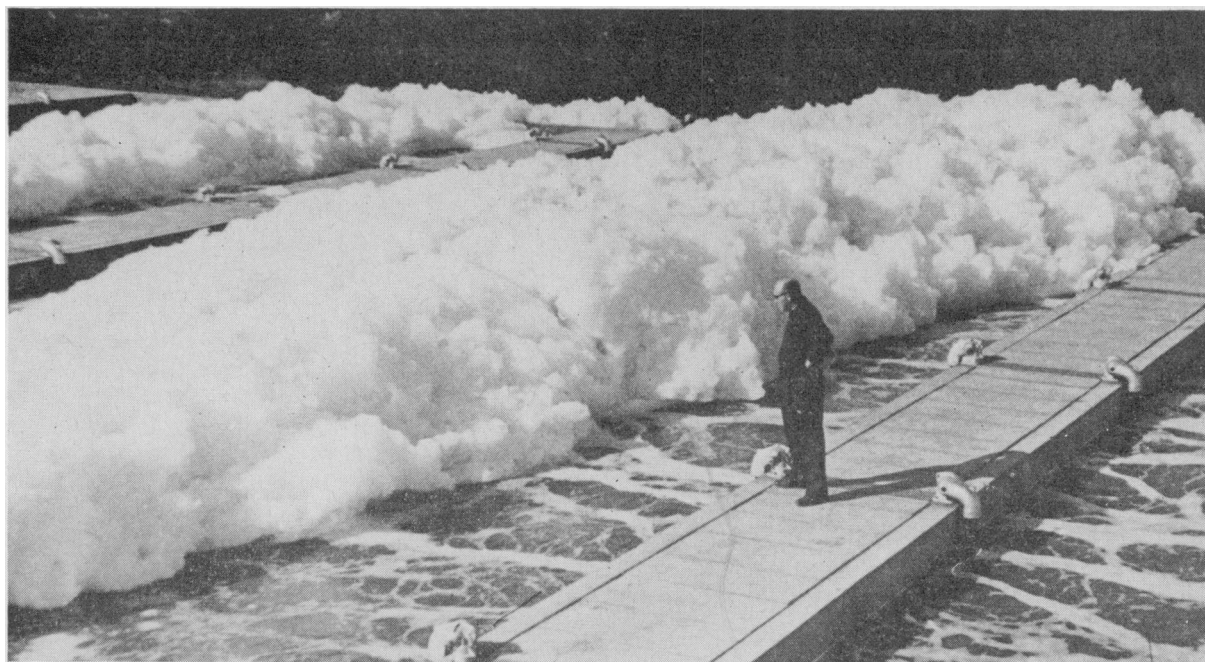


Figure 3. Picture of frothing conditions of sewage plant at Benton Harbor, Mich. The exact causes of this foaming condition are not known but synthetic detergents have been implicated. Analysis has shown large quantities of detergents in the foam.

such materials as DDT in water may not be significant from the standpoint of human physiological effects, concentrations below 1 p.p.m. of chlorinated insecticides are toxic to fish (16); toxaphene (17) has been reported to be lethal to fish in 10 days at less than 6 p.p.b. concentration.

Synthetic Detergents

Synthetic detergents as potential water polluting materials are receiving much more attention since the occurrence of excessive foaming at water plants in Kansas and West Virginia (18, 19). These materials are unique in that virtually all of the product ends up as waste. A review of the detergent problem has been published (20). Foam materials from Wheeling, W. Va., were identified by means of infrared spectrums as originating from synthetic detergents of the alkylarylsulfonate type (anionic). (Approximately 80 percent of all detergent produced is of this type.) The striking resemblance of the infrared spectrums of the pure material and materials recovered from the foam (fig. 2) leaves no doubt as to the presence of surfactant in the foam. Tastes, odors, and interference with water treatment

have been ascribed to the presence of these materials in concentrations of a few parts per million. This concentration does not normally occur in water. These substances are resistant to biological forces of purification in the stream and will survive usual water treatment processes although they are readily adsorbed by active carbon. Small concentrations have been isolated from tap water, and the materials undoubtedly constitute a portion of our daily organic intake with drinking water.

Sewage treatment plants have experienced troublesome foam problems. Foaming may be due to causes other than detergents, but in a number of instances high concentrations of anionic materials have been present in the foam materials. Samples of the foam from the Benton Harbor, Mich., plant (fig. 3) were shown by infrared methods to be high in detergent materials. A report (21) has described the difficulties of the frothing at this plant.

Natural Materials

Products of natural origin in water are frequently responsible for taste and odor difficulties. In addition, kills of wild and domestic

animals have been associated with blooms of certain toxic algae. Odors of these materials are often described as musty, earthy, pigpen, geranium, fishy, and cucumber. Many of these odors have been associated with algae. Silvey (22, 23) has proposed that actinomycetes are responsible for musty and other odors in various waters, particularly in the southwest. The chemicals elaborated by the organisms have not been identified. A musty component has been recovered from numerous waters in the Cincinnati laboratory by extended purification following steam distillation of the neutral materials. This material constitutes a very small percentage of the total extract but possesses an extremely intense odor.

Waters from various surface sources have contained substantial quantities of carbonyl compounds. Such materials as organic acids, ketones, and aldehydes may result from natural decay, oxidation, and life and death processes of plants and other aquatic life. Organic acids may also represent an intermediate step in the oxidation of industrial materials, including hydrocarbons. Hence identification of these materials does not reveal their origin.

Much remains to be learned of all the effects natural products have on the pollution of our water resources. One objective of studies in progress at the Robert A. Taft Sanitary Engineering Center is the determination of the role of algae as sources of taste and odor. Further chemical studies are being pursued in areas experiencing difficulties in taste and odor where nonindustrially polluted waters serve as a source of supply.

Summary

Water quality is seriously affected by contamination from organic materials. Both drinking water and industrial supplies are impaired. Apart from the nuisance and deprivation caused by effects on drinking water, it is conceivable that physiological effects may result from high concentrations of these materials in public water supplies. At what concentration materials such as those isolated from drinking water constitute a hazard is not known. Many of the organic materials in water have not yet been isolated or identified.

Methods for studying these materials have been indicated and some of the results outlined. In view of the increased industrialization, increased water use, and the present lack of knowledge of natural pollutants, the total effects of organic chemicals on water quality and means for the control of the materials demand increased attention.

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technical publications

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